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FE-CR-AL ALLOY WITH EXCELLENT DURABILITY AND CATALYST CARRIER USING IT

[Taikyuseini Sugureta Fe-Cr-Al gokin oyobi sore o mochiita shokubai tantai]

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Claims

1. An Fe-Cr-Al alloy with excellent durability, that contains

C: 0.05 wt% or less

Si: 0.2 wt% or less

Mn: 1.0wt% or less

P: 0.040 wt% or less

Cr: 18-28 wt%

Ni: 0.3 wt% or less

Cu: 0.3 wt% or less

Al: 1-10 wt%

N: 0.02 wt% or less

where the Si, Mn, P, Ni, and Cu satisfies Formula (I) below, with the remainder comprising Fe with inevitable impurities.

$$9.5\ Si + 2Mn + 10P + 3.6\ (Ni+Cu) - 2.5 \leq 0 \qquad (I)$$

2. An alloy wherein the alloy described in Claim 1 contains 0.01-0.20 wt% La.

3. An alloy, wherein the alloy described in Claim 1 or Claim 2 contains 1, 2, or more of the following: a total of 0.01-0.20 wt% of lanthanides other than La , 0.05-0.5 wt% Y, and 0.01-0.3 wt% Hf.

4. An alloy, wherein the alloy described in any of Claims 1-3 additionally contains 1.0 wt% or less of a total of at least 1 species selected from Ti, Nb, Ta, and V.

5. An alloy, wherein the alloy described in any of Claims 1, 3, or 4 additionally contains 0.01-1.0 wt% Zr.

6. An alloy, wherein the alloy described in any of Claims 1-5 contains 0.0005-0.01 wt% B.

7. A catalyst carrier that is assembled using a foil prepared from the alloy described in any of Claims 1-6.

[0001]

Technical field of the invention

The present invention pertains to an oxidation resistant alloy steel typified by metallic materials for catalyst carriers such as exhaust gas converters, for example; in particular it pertains to materials with excellent durability at high temperatures of 1000°C and above.

[0002]

Prior art

Exhaust gas cleaning catalytic converters are used to detoxify toxic gases such as NO_X and CO, for example, that are produced when fuel and air are mixed and combusted. This catalytic conversion is an exothermic reaction and thereby raises the temperature of the converter. Recently, there have been many cases of positioning converters near the combustion area in order to increase the efficiency of the catalytic reaction, so that the catalytic reaction is made to occur in the high temperature exhaust gas; this is an extremely severe temperature environment for converter materials in terms of thermal shock and exhaust gas pressure. Accordingly, the materials for catalytic converters that are used under such conditions are mainly metallic materials such as Fe-Cr-Al alloy, which has excellent oxidation resistance, because ceramics, which are vulnerable to thermal shock, do not stand up under use.

[0003]

Problems to be solved by the present invention

Nevertheless, conventional Fe-Cr-Al alloy have inadequate durability as materials for catalytic converters when used as the alloy foil under high temperatures exceeding 1000°C, which are the recent maximum temperatures, and the actual situation is that they do not stand up under use, for the honeycomb foil becomes brittle at high temperature and breaks, for example. Accordingly, the object of the present invention is to offer an Fe-Cr-Al alloy with excellent durability that solves the problems of the prior art as described above, as well as a catalyst carrier to be used with it.

[0004]

Means to solve the problem

The invention is an Fe-Cr-Al alloy for catalytic converters with excellent durability that has improved the problems described above for conventional materials used for catalytic converters. The essence of the present invention is as follows. More specifically, the present invention is an Fe-Cr-Al alloy with excellent durability that contains

C: 0.05 wt% or less

Si: 0.2 wt% or less

Mn: 1.0wt% or less

P: 0.040 wt% or less

Cr: 18-28 wt%

Ni: 0.3 wt% or less

Cu: 0.3 wt% or less

Al: 1-10 wt%

N: 0.02 wt% or less

for which the Si, Mn, P, Ni, and Cu satisfies Formula (I) below, with the remainder comprising Fe with inevitable impurities.

$$9.5\ Si + 2Mn + 10P + 3.6\ (Ni+Cu) - 2.5 \leq 0 \qquad (I)$$

[0005]

In addition to the aforementioned ingredients, the invented alloy may also contain at least 1 type of group selected from groups (a), (b), (c), (d), and (e) below. However, the combined presence of (a) and (d) is excluded.

(a) La: 0.01-0.20 wt%

(b) 1, 2, or more of the following: a total of 0.01-0.20 wt% of lanthanides other than La , 0.05-0.5 wt% Y, and 0.01-0.3 wt% Hf.

(c) 1.0 wt% or less of a total of at least 1 species selected from Ti, Nb, Ta, and V.

(d) Zr: 0.01-1.0 wt%

(e) B: 0.0005-1.0 wt%

[0006]

The present invention also offers a catalyst carrier that is assembled using a foil prepared from the aforementioned alloys.

[0007]

Operation

The following statements explain the present invention in greater detail. The exhaust gas cleaning catalytic converter temperature, when the converter placed in a position near the combustion environment in order to cause a catalytic reaction to occur in the high temperature exhaust gas, is 1000°C or greater. Therefore, with regard to Fe-Cr-Al alloy that is used conventionally at temperatures of 1000°C or less, the present situation is that the difference between high temperatures and low temperatures is extremely great, so that due to the thermal stress that up until now had not been much of a problem, the honeycomb foil is subjected to grain boundary cracks, and then breaks, or the oxidation resistance above 1000°C is insufficient, so that abnormal oxidation occurs over a short period of time, and the converter can no longer withstand use. The inventors investigated the causes of intergranular fracture, and as a result determined that intermetallic compounds deposited in the grain boundary are the cause of grain boundary cracks, and as a result of investigating the effect of alloy elements on the deposition of these intermetallic compounds, discovered that Si, Mn, P, Ni, and Cu are particularly harmful, and that the metallic compound production effect of each of these elements is different. The coefficient for component elements in Formula (I) expresses this relation quantitatively, and once the relation of Formula (I) is satisfied, it is possible to prevent deposition of intermetallic compounds at the grain boundary, which is the cause of high temperature brittleness.

[0008]

The following statements explain the operation of the alloy elements.

[0009]

C and N: In ferrite-type stainless steel the solid solution limit of both C and N is low, and they are deposited mainly as carbides and nitrides, causing degradation of corrosion resistance and significantly reducing the tenacity and durability of the steel plate. In particular, N forms nitrides with Al, thus decreasing the amount of effective Al (solid solution Al), and since gigantic nitrides cause defects during foil manufacturing this results in significant degradation of the yield, so that it is desirable to reduce the content as much as possible; but in consideration of industrial and economical ingot technology, the upper limits have been set at 0.05 wt% for C and 0.02 wt% for N.

[0010]

Si, Mn, P, Ni, Cu: These elements promote the deposition of intermetallic compounds at the grain boundaries of honeycomb foil, and they promote brittleness at high temperature, so that it is desirable to extremely reduce their content. In order to suppress intermetallic compounds, when these elements are not present together, it is necessary for Si to be 0.2 wt% or less, Mn 1.0 wt% or less, preferably 0.40 wt% or less, P 0.040 wt% or less, preferably 0.030 wt% or less, Ni 0.3 wt% or less, Cu 0.03 wt% or less. However, if the content of these elements is excessively reduced, the refining costs will increase, which would be uneconomical. Therefore it is necessary for the production of intermetallic compounds to be suppressed by a balanced reduction of these elements. The intermetallic compound production effect of each element is different, quantitatively expressed by Parameter A. More specifically:

$$A = 9.5\,Si + 2\,Mn + 10\,P + 3.6\,(Ni+Cu) \quad - 2.5$$

With regard to an Fe-Cr-Al alloy having the ranges: C: 0.05 wt% or less, N:0.02 wt% or less, Si: 0.2 wt% or less, Mn: 0.2 wt% or less, P: 0.04 wt% or less, Ni: 0.3 wt% or less, Cu: 0.3 wt% or less, Cr: 18-28 wt%, and Al: 1-10 wt%, Parameter A and the intermetallic compounds deposition phase rate, and

the honeycomb breakage relation is taken. The results are shown on Figure 1. Figure 1 demonstrates that when Parameter A is 0 or less, the deposition phase will be approximately 0 and there will be no honeycomb breakage. Accordingly, in order to suppress honeycomb breakage, the ingredient range has been limited, and it is also necessary to satisfy Formula (I).

$$9.5\ Si + 2Mn + 10P + 3.6\ (Ni+Cu) - 2.5 \leq 0 \qquad (I)$$

Formula (I) expresses the necessary conditions for suppressing the deposition of intermetallic compounds. It is possible to suppress the formation of intermetallic compounds with good efficiency by suitably reducing each element to within the ranges that satisfy this formula, and thus it is possible to prevent honeycomb breakage.

[0011]

Cr: It is necessary to add 18 wt% or more Cr in order to make the effect, sufficiently manifest, because this is an element that improves oxidation resistance. The oxidation resistance improving effect of Cr is increased as the amount added is increased, but if it exceeds 28 wt% the tenacity and ductility will decline and there will be deviations from manufacturability, so that the range is limited to 18-28 wt%.

[0012]

Al: Al is an element that is necessary and indispensable for maintaining oxidation resistance, and as increasing amounts are added a material is formed that withstands use for long periods of time and at high temperatures. It is necessary that 1 wt% or more be used in order to make its effect sufficiently manifest. However, if the content exceeds 10 wt%, there will be deviations from machinability during cool periods, and cracks will form during honeycomb machining, so that the upper limit is 10 wt%, and

the range is 1-10 wt%. Here the amount of Al may be adjusted. When an alloy containing 7 wt% or more Al is formed as an ingot, the tenacity will be low and manufacturing will be difficult, so that the Al is made to adhere by a method such as plating, for example, onto an alloy of suitable composition, and the Al is diffused by heat treatment.

Zr: Zr has the effect of fixing and detoxifying the S that is deleterious to oxidation resistance, and also has the effect of fixing N and suppressing the production of massive AlN. A content of at least 0.01 wt% or more is needed in order for these effects to be exhibited. But if the content is greater than 1.0 wt%, tenacity will decline and manufacturability of the steel will be significantly degraded, so that the upper limit is 1.0 wt%, and the range is limited to 0.01-1.0 wt%.

[0013]

Lanthanoids, Y, Hf: These elements have the effect of improving oxidation resistance through improving the adhesion of the oxide film formed at high temperature on the Fe-Cr-Al alloy. It is desirably for these element to be abundant because of this effect, but because the solid solution limit with regard to Fe-Cr-Al alloy is low, if the content exceeds the solid solution limit they will be deposited at the grain boundary and machinability will be impaired, so that the respective upper limits are La: 0.01-0.20 wt%, lanthanoids other than La: 0.20 wt%, Y: 0.50 wt%, Hf: 0.3 wt%; the range of total lanthanoids is 0.01-0.20 wt%, Y:0.05-0.5 wt%, Hf: 0.01-0.3 wt%.

[0014]

Ti, Nb, Ta, V: these elements have the effect of detoxifying N, which forms AlN, ablates Al, and degrades oxidation resistance, but if an excess is contained, manufacturability is reduced, so that the upper limit is set at 1.0 wt% for a total content.

[0015]

B: B strengthens the grain boundary by removing impurities that are the cause of intergranular fracture at high temperatures, and thus has an extremely significant effect for reducing brittleness at high temperatures. In order that this effect may be sufficiently exhibited, the content must be 0.0005 wt% or greater. However, if the content exceeds 0.01 wt%, a counterproductive tendency is observed wherein embrittlement at high temperature is assisted; therefore, the upper limit is set at 0.01 wt%, and the range is established at 0.0005-0.01 wt%.

[0016]

The invented Fe-Cr-Al alloy is to be used by conducting an investigation of the components in a melt condition, casting into an ingot or slab, subjected to hot rolling and annealing, then subjected to repeated cycles of cold rolling and annealing, and used as a coil or cut plates of the necessary thickness; or it may be made into an article that has been subject to adhesion of Al or an Al alloy containing the necessary elements, either by a cladding treatment or plating treatment, for example, onto the surface of the alloy of suitable components in coil or cut-plate form, and this article is then subjected to a suitable heat treatment such that the elements are dispersed, and then used as a coil or cut plates having a surface with the chemical structure stipulated in the claims.

[0017]

Coils or cut plates of the alloy composition obtained as described above can be used in applications where durability is required. In particular, they are useful as catalyst carriers for exhaust gas converts,

for example. At this time, the alloy steel is formed into a foil, which is formed into a honeycomb structure by any means such as welding, brazing, or mechanical joining, for example.

[0018]

Application examples

The following statements describe the present invention more specifically with relation to application examples.

Application Example 1

A honeycomb was prepared from foil that had been manufactured from the alloy steels having the compositions shown in Table 1. The existence of breakage after durability testing of honeycomb-finished articles of both the application examples and comparative examples is shown in Table 1. With regard to example A7 of the present invention and comparative example B2, Al was plated on Fe-Cr-Al alloy plate of suitable components, which was then subjected to diffusion treatment in an inert gas, yielding alloy plates of standard composition. Said alloy plates were subjected to cold rolling to 50 microns, and the aforementioned bright annealing was conducted. Concerning the alloys other than the two just mentioned, they were made into ingots by vacuum dissolution, and then subjected to repeated cycles of hot rolling, annealing, cold rolling, and annealing, then cold rolled to 50 microns, after which bright annealing was conducted.

[0019]

The honeycomb durability test was conducted as follows. Honeycombs that had been prepared by winding flat plates and wavy plates, and then fixing this with spot welding, were subjected to a test with

repeated cycles of increased temperature, with the temperature raised to 1100°C and then decreasing to room temperature. Afterwards the samples were evaluated by assigning X's or hollow circles, according to whether honeycomb breakage had or had not occurred, based upon disassembly and inspection. It was demonstrated that, compared with the comparative examples, the examples of the present invention did not have honeycomb breakage, and were thus suitable as materials for use for catalytic converters with excellent durability.

[0020]

Table 1

Table 1 (wt %)

	C	N	Si	Mn	P	Ni	Cu	Cr	Al	REM Y, Hf	Zr	Ti, Nb, Ta, Y	B	1
A1	0.005	0.007	0.11	0.12	0.021	0.64	0.03	20.5	3.5	Y :0.1	–	–	0.0012	○
A2	0.006	0.011	0.08	0.10	0.022	0.61	0.01	18.5	3.5		0.3	Ti:0.3	–	○
A3	0.008	0.008	0.11	0.33	0.027	0.12	0.04	25.7	5.3	REM:0.1 Hf :0.1	–	Nb:0.1 Ta:0.2 Y :0.1	–	○
A4	0.006	0.012	0.06	0.33	0.015	0.11	0.10	20.7	6.5	Y :0.3	0.2	Ti:0.05	0.0081	○
A5	0.007	0.009	0.13	0.09	0.014	0.05	0.03	20.7	5.3	REM:0.06	–	Ti:0.05	–	○
A6	0.007	0.008	0.06	0.38	0.022	0.07	0.06	27.5	3.3	REM:0.16	–	Ta:0.35	–	○
A7	0.006	0.009	0.07	0.38	0.021	0.06	0.03	20.2	6.9	Y :0.5	0.5	Y :0.02	0.0032	○
B1	0.005	0.008	0.39	0.15	0.021	0.12	0.10	20.2	3.5	–	–	Ti:0.35 Ta:0.37	–	×
B2	0.008	0.012	0.25	0.35	0.026	0.61	0.02	20.5	7.8	REM:0.15	–	–	–	×
B3	0.005	0.005	0.26	0.16	0.025	0.15	0.61	25.0	5.2	–	0.3	–	–	×

Key: 1 Existence of honeycomb breakage

[0021]

Effect of the invention

The present invention makes it possible to obtain a Fe-Cr-Al alloy with excellent durability, in order to resist intermetallic compound grain boundary deposition, by controlling the content of Si, Mn, P, Ni,

and Cu in the Fe-Cr-Al alloy; a catalyst carrier that uses this alloy foil does not break even at high temperatures, in comparison with conventional articles.

Brief explanation of the figures

Figure 1 is a graph of the correspondence between parameter A and deposition intermetalic compound phase rate and the honeycomb breakage.

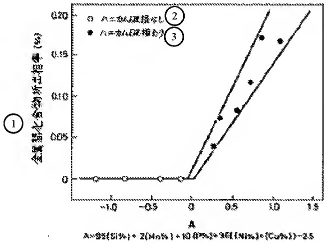

Figure 1

Key: 1 Intermetallic compound deposition phase rate (%)

2 No honeycomb breakage

3 Honeycomb breakage